Recycling of Elium CFRPs for high temperature dissolution: A study with different solvents

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Abstract

Due to the all-encompassing problem of recycling conventional thermoset composites, which neither leads to sufficient matrix recovery nor to the recovery of fibres in satisfactory quality, new thermoplastic matrix systems are being explored for special interest against the background of closed loop recycling. For this reason, the Institute for Polymer Materials and Plastics Engineering at the TU Clausthal is researching the novel matrix system Elium 150 from the French manufacturer Arkema [1, 2]. This system, which is infusible and curable at room temperature, is characterised by a processing similar to conventional thermosetting resin systems with comparable mechanical properties, which leads to a high market potential. In order to prevent the accumulation of waste without a satisfactory recycling method for this material, we are already investigating to develop recycling processes at its market introduction phase. A dissolution based process has been developed which, at room temperature separates the matrix from the fibres within 24 hours [1]. This process allows to recover both the fibres in undamaged form (scrims) and the matrix as well. Both the matrix and the fibre properties of the recycled products can be considered comparable to virgin materials [2].

In order to shorten the process time, the use of higher temperatures for dissolution is a common practice. Therefore as a quicker recycling method the use of microwaves as possible heating source is our next objective. A key factor for this is a temperature resistant solvent. As acetone being volatile raises safety concerns at high temperatures and hence is not a suitable solvent for use in the microwave. Such being the case, this article investigates temperature-resistant solvents, which can be the medium for recycling Elium CFRPs via microwave heating. Solvents being considered are in particular acetophenone, xylene and ethyl acetate to determine their suitability.

1 Introduction

The aim of recycling fiber reinforced composites is to save costs, reduce energy consumption and waste with regards to environmental aspects within the aegis of circular economy concept [1]. Against this backdrop and the increasing use of fiber plastic composites in the automotive, aerospace and wind power industries [1], the new matrix material Elium produced by the French company Arkema is researched for developing a novel recycling process. Elium 150 is a thermoplastic matrix material that can be infused and polymerized at room temperature [2]. Since the processing and mechanical properties of Elium are similar to those of conventional thermoset systems, this thermoplastic system has a high market potential.

One method of recycling fibre reinforced plastic composites is via dissolution [3,4]. Up to now, research has been conducted on a dissolution process with acetone, in which Elium separates from the fibres within 24 hours at room temperature. The fibres remain undamaged and over 80% of the matrix can be recovered. Furthermore, hardly any deterioration of the interlaminar properties could be detected [3,4].

However, acetone being volatile is not temperature resistant, which would be a favourable feature necessary for shorter process times. For a faster recycling process, microwaves-based heating should serve as a possible route. In this article, several solvents are tested for their suitability with regard to increased process temperature and compared. On one hand, these were selected according to temperature resistance and on the other hand according to environmental aspects. The influence of the solvents on the matrix and on the fibres has been evaluated and presented here.

2. Experimental section

2.1 Materials

The composites were processed with carbon fibres and Elium 150 produced by Akema. Elium is polymerized by adding 2.5 wt% of AkzoNobel's initiator Perkadox CH-50X. A 0/90° scrim of carbon-fibres with an aerial weight of 636 gsm from SAERTEX (B-C-636 gsm, width: 1270 mm) was used as reinforcement for the composite. In the production of the composites Frekote 770NC from Henkel was used as a mold release agent. For the solvent comparison acetone (99.5 % purity) was tested against, acetophenone (99 % purity), ethyl acetate (99.5 % purity) and xylene (99 % purity) due to their comparatively lower environmental influences and usability at higher temperatures. Isopropanol (99 % purity) was used to extract Elium from the acetophenone by precipitation.

2.2 Composite processing

In order to process the carbon fibre reinforced plastics (CFRP) laminates (400 mm x 300 mm) with two layers of fabrics (Fibre vol. fraction: 45 % approx.) was processed via, vacuum-assisted-resin-infusion (VARI) process. For this, a glass plate was coated with Frekote 770NC. The Elium 150 was manually mixed with the Perkadox CH 50-X and then degassed under vacuum for 10 minutes. The infusion was carried out along the longer side of the fibre preform as has been done so far in-house [3,4]. Next, after the infusion is completed, the laminate was cured for 90 minutes at 65° C under a thermal blanket. Finally, the samples were machined into the size of 65 mm x 30 mm before the dissolution process.

2.3 Dissolution Process

For the preliminary dissolution tests, polymerised Elium without fibres is used as granulates. For its preparation first Tacky-Tape (DB-90 G Tacky Tape, WELA Handelsgesellschaft mbH) is used to stick a frame (300 mm x 200 mm) onto a glass plate. Then bulk Elium was poured to achieve a thickness of 4 mm. After 24 hours at room temperature, the polymerised plate was broken into larger pieces by hand and further crushed to particles averaging 4–8 mm in size in a granulator (Dreher, type S 26/26 GF).

The pure, cured Elium in granular form was dissolved in the different solvents (with the ratio Elium:solvent of 1:10 and 1:20) at room temperature to determine the time and solvent ratio required for the dissolution process.

In the second step, the composites were examined. First the weight and geometry of the CFRP samples were measured and then the composites were placed in a sealed container with an appropriate solvent. All dissolving processes with CFRP were carried out at room temperature and a ratio of 1:20 as this parameter showed the best results with pure Elium (*Fig. 1*). After 24 hours the fibres were removed from the container and the samples solved in acetone and ethyl acetate dried for 8 hours at 65° C in a vacuum oven, whereas the fibres immerged in acetophenone were dried at 90° C in the vacuum oven to remove any residual solvent. The higher drying temperature of 90° C for acetophenone was chosen because of its high boiling point (202° C). In the case of acetone and ethyl acetate, the matrix was recovered by evaporating the solvents and then post-dried under the above-mentioned conditions. Due to its high boiling point, from acetophenone, the Elium was precipitated with dropping isopropanol (ratio acetophenone:isopropanol : 1:20) and then filtering out and further drying the reclaimed Elium. Finally, the weight of the fibres and the recovered matrix were measured to quantify the amount of residual matrix adhering to the fibres after the dissolution process.

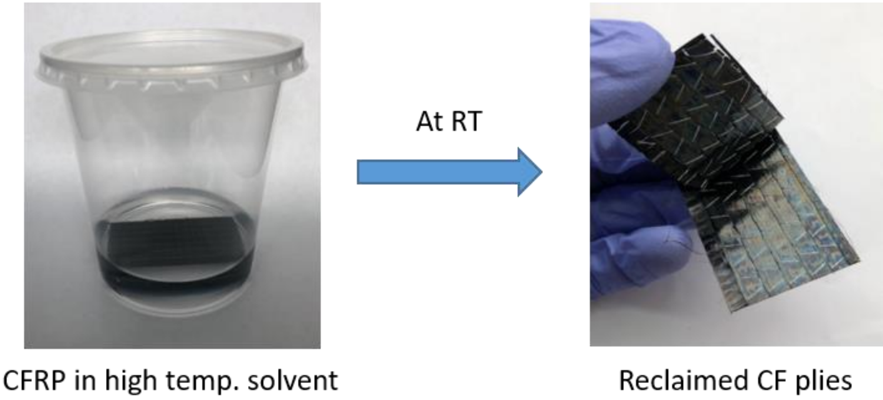

Fig. 1: Dissolution process of the CFRP

2.4 Characterization techniques

The thermal analysis of the matrix after the dissolution process was carried out with differential scanning calorimetry (DSC, DSC 2920 TA instruments) according to DIN EN ISO 11357-1 and via thermogravimetric analysis (TGA, TGA 2950 TA instruments) according to DIN EN ISO 11358 under nitrogen atmosphere. The DSC is used to determine the glass transition temperature, allowing conclusions to be drawn about the molecular structure as well as the thermal applicability.The DSC measurements were taken following the heat-cool-heat process from –20° C to 200° C (heating ramp: 10^{o} C/min, cooling ramp: 50^{o} C/min). Furthermore, the values of the 2^{nd} run were considered for the glass transition temperatures for evaluation to exclude the thermal history. The TGA measurements were performed at a heating rate of 10^{o} C/min from 25° C to 600° C. For the evaluation, the 5 % and 10 % thresholds of weight loss were considered.

The single fibre tensile tests (SFT) were carried out with 40–50 mm long fibres to compare the strength of the recycled fibres with the original fibres according to ISO 11566. Single fibres were separated and glued between two sheets of paper frames with the Araldite AW4859/HW4859 adhesive. The free length between the glued surfaces was 30 mm. Thereafter this fixture was clamped to the Zwick/Roell ZMART.PRO tensile testing machine with a load cell of 20 N and a preload of 0.001 N. In order to determine the influence of the solvents on the fibres, the failure load of the recycled fibres was determined. Besides the measured values were evaluated according to the Weibull analysis as common practice. Data of 20 fibres for each solvent were recorded for statistical reasons.

3. Results and discussion

3.1 Quantitative analysis of Elium recovery

To find out which solvent is suitable for dissolving Elium, a preliminary test is performed with xylene, ethyl acetate and acetophenone, which has been compared with the established process with acetone [4]. The solvents under consideration have been selected based on several reasons. Acetone serves as a reference for the already established Elium recycling at room temperature [4]. Ethyl acetate has a higher boiling point than acetone and at the same time a better environmental compatibility, therefore it is considered [5]. With toluene and acetophenone, two solvents are considered, which have higher boiling points and therefore preferable for high temperature dissolution. According to Evchuk et al. [5], all solvents considered can dissolve PMMA, which is chemically comparable to Elium.

The determined time periods for the complete dissolution of polymerised bulk Elium in the solvents are shown in *Table 1*.

Tab. 1: Time for complete dissolution of bulk Elium

Elium:solvent ratio (RT)	Acetone	Acetophenone	Ethyl acetate	Xylene
1:20	24 h	48 h	24 h	> 72 h
1:10	48 h	72 h	24 h	> 72 h

In general, a shortening of the time to complete dissolution of the Elium can be seen with increasing Elium solvent ratio, which is why the ratio 1:20 was chosen for the composite tests. Larger ratios do not seem worth considering due to the large amounts of solvents required. In Xylene, different to observations in other publications [5], Elium did not completely dissolve after more than 72 hours, so Xylene was not considered for further investigations. Ethyl acetate and acetone seem to dissolve Elium equally well at a ratio of 1:20, while acetophenone needs more time to dissolve the bulk.

In the tests with composites, both the amount of recycled matrix and the amount of matrix remaining on the fibres after 24 hours for acetone and ethyl acetate can be considered comparable (*Fig. 2*). Thus, ethyl acetate can be considered an environmentally worthy alternative to acetone, at least regarding its dissolution and recovery behavior.

Interesting and unexpected after the pre-tests is that the recovered amount of matrix in acetophenone is slightly more than that of the other solvents.

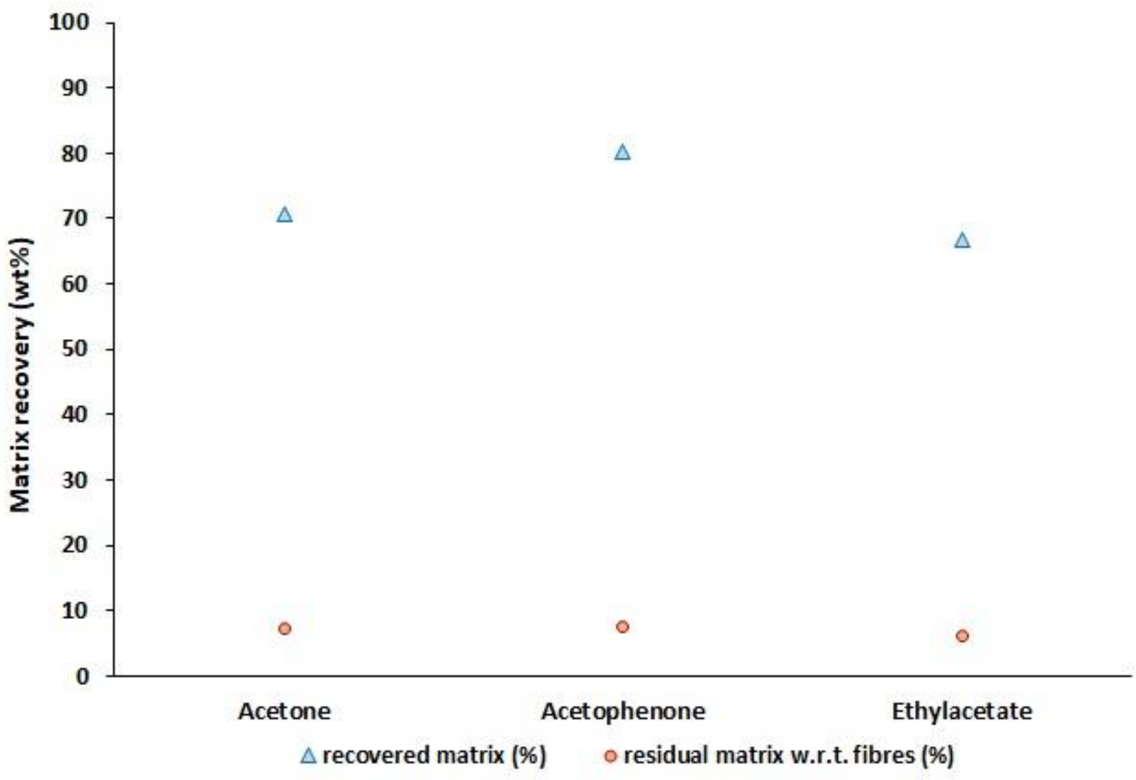

Fig. 2: recycled matrix and matrix remaining on the fibres

3.2 Thermogravimetric analysis (TGA)

The TGA measurements were used to investigate the extent to which the solvents have an influence on the thermal stability of the recycled Elium. The thermal degradation of the virgin Elium, and the Elium dissolved in acetone as well as ethyl acetate were found to be very similar. The Elium dissolved in acetophenone has a significantly higher stability than the others (*Fig. 3 and Table 2*). The onset of degradation of Elium is at approx. 90° C [4]. So, the samples with acetophenone were dried for 8 h at 90° C (due to its high boiling point) under vacuum which translates to temperatures higher than this under atmospheric pressure. This would in turn reduce the viscosity and thus increase the molecular movement of the specimen, which likely leads to the possibility of the remaining monomers continuing to react further, thereby introducing an additional post-curing effect. This might result in longer chains, increased molecular weight, as has been already observed by Madorsky [7] for PMMA, thus resulting in an increased thermal stability. However, this assumption is part of future research being carried out in-house.

Another possibility is that given the high boiling point of acetophenone, 8 h at 90ºC under vacuum is not sufficient to remove all the solvent thus pushing the onset of degradation at higher temperature as reflected here.

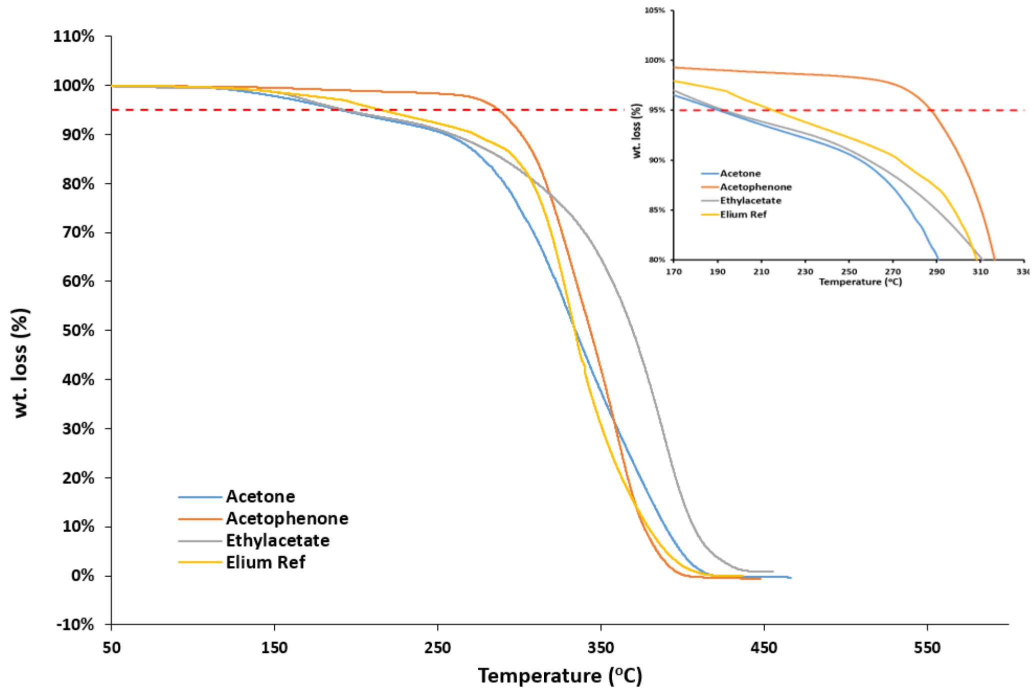

Fig. 3: TGA measurements

Table 2: 90 wt% and 95 wt% thresholds of the TGA measurements

Sample	95wt% threshold, °C	90wt% threshold, °C
virgin Elium [1]	215	273
recycled by acetone [1]	190	255
recycled by ethyl acetate	195	259
recycled by acetophenone	288	301

3.3 Differential scanning calorimetry (DSC)

The DSC analysis was performed to further investigate the influence of solvents and process parameters on the glass transition temperature and thus the maximum application temperature of the recycled material. There is a clear difference between Elium recycled with ethyl acetate and that recycled with other solvents (Table 3).

Table 3: Variation in glass transition temperature from DSC of Elium reclaimed after recycling with the different solvents

Sample	**T_g (mid-point, ^{o}C)**
virgin Elium [1]	99.3
recycled by acetone	115.1
recycled by ethyl acetate	100.6
recycled by acetophenone	115.6

T_g of ethyl acetate is in the range of virgin Elium, whereas the values for both acetone and acetophenone are increased by about 15°C. The higher T_g when recycling with acetophenone is, as already described, is likely due to the post-curing reaction during the evaporation process of the solvent at 90° C under vacuum. As described in previous research [4], the increase in T_g during recycling with acetone is mainly due to the solution polymerization of Elium during the recycling process. However, from the current measurements it is interesting to note that this phenomenon does not seem to be evident when recycling with ethyl acetate. Nevertheless, even when recycling with ethyl acetate, there is no reduction in the thermal applicability of the recycled material compared to virgin Elium.

3.4 Single fibre tensile test

The breaking strength of carbon fibres generally depends on their length. The longer the fibres are, the more defects are present. This is more likely to cause fibres breakage [8]. The values for breaking strength of the fibres have been investigated using the single fiber tensile test and thereafter evaluated using the Weibull analysis as is common practice. According to previous publications as well as common standard the point at which 63 % of all fibres tested failed was considered [3,4].

Not much has changed in terms of breaking strength within the statistical tolerance. The different solvents had barely any influence on the mechanical properties of the fibres and can be regarded as approximately similar in structural integrity to the virgin fibres from the fabric (Fig. 4).

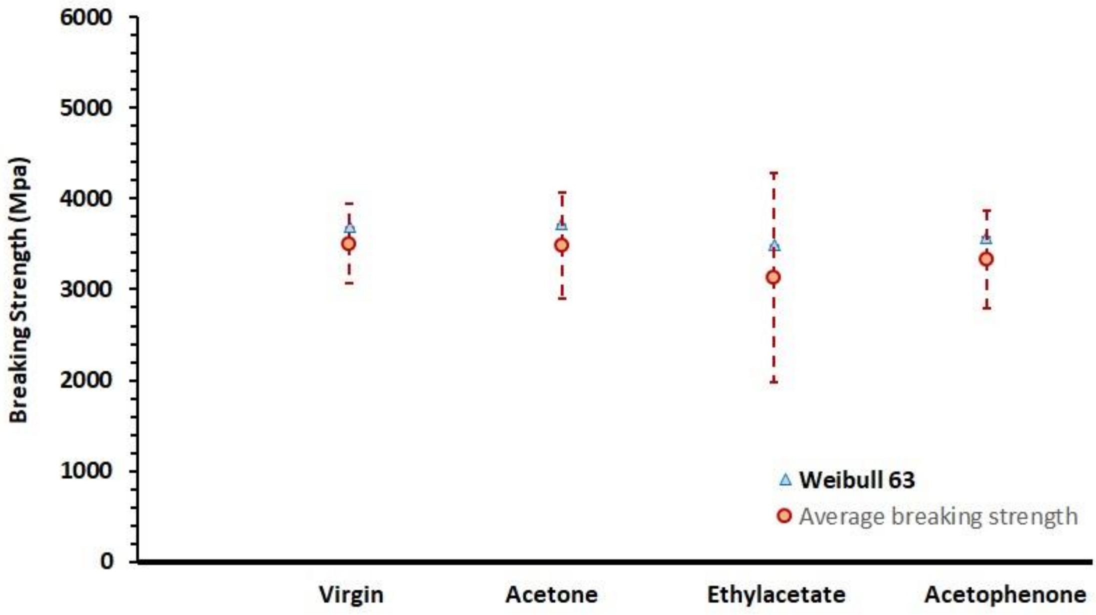

Fig. 4: Breaking strength, Weibull 63 % -value

4. Conclusion

It can be stated that an Elium:solvent ratio of 1:20 is recommended for a time saving dissolution process. A lower ratio extends the solution times noticeably. At the same time xylene can be characterized as unsuitable for dissolving Elium and thus for recycling Elium CFRP.

Ethyl acetate represents an environmentally friendly alternative to the established room temperature-based recycling process using acetone as solvent. Both, the amount of Elium recovered, and the amount of Elium remaining on the fibres are observed to be comparable. Furthermore, both the thermal stability and the influence on the structural integrity of the fibres can be regarded as very similar. However, in terms of glass transition, Elium recycled with ethyl acetate is more comparable to virgin Elium than it is to Elium recycled with acetone.

Acetophenone offers high potential as a solvent for use in recycling processes at higher temperatures, which are currently the subject of ongoing in-house research. Especially the higher thermal stability of the recovered Elium due to the change in the recovery process is remarkable bonus when the solvent is used in high temperature dissolution like using microwave ovens as the heat source.

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